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Network Model for the Entangled Polymer Melts : A Review

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Abstract

This paper reviews the research on network models of the entangled polymer melts from kinetic network, affine and nonaffine transient network, and complex network, respectively. The emphasis is placed upon the complex network model, which is a new method to study the rheology of the entangled polymer melts.

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Keywords: entangled polymer melts; kinetic network; affine transient network; nonaffine transient network; complex network

1. Introduction

In recent years, more and more things made of plastic, rubber and fibre have been widely used in our everyday life which arouses our considerable interests in the study of the characteristics and structures of polymer melts. At very low shear rate, the melts behave as a Newtonian fluid. However, when the shear rate is increased, the viscoelastic behaviour becomes nonlinear. It is well known that the nonlinear viscoelastic behavior of polymer melts is often attributed to interactions between long-chain molecules, which caused by entanglements of long-chain molecules [1]. These interactions are frequently modeled as networks of junctions, which translate, rotate and deform with the liquid. Therefore, the rheology of entangled polymer melts under high shear rates has been discussed theoretically by many authors.

Firstly, a kinetic network model has been developed to describe the nonlinear rheological behavior of entangled polymer solutions and melts in either steady state or transient flows. This model is based on the concept of flow-induced structure variation, controlled by the simultaneous existence of entanglement loss and regeneration. Different kinetic rate equations have been proposed by Marrucci model [2], Acierno model [3], Mewis-Cleyn model [4], Liu model [5], Mewis-Denn model [6], etc. In 1956, Lodge [7] proposed rubber-like model, which modeled entanglement network as junctions of constant population. In 1973, Marucci et al. [2] modeled as temporary junctions whose kinetics is governed by invariants of the extra stress tensor and thermal motion of the molecules.

Secondly, Giacomini and Jeyaseelan [8–9] use transient structural network theory with the upper convected Maxwell model to describe the rheological behavior of several kinds of polyolefin melts in large amplitude oscillatory shear, which is a simple force field. Subsequently, Zhang [10–13] proposes the precision of the nonaffine

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model (the Gordon-Schowalter convected Maxwell model) for polymer melt in large amplitude oscillatory shear field is proved to be higher than that of the affine model (the upper convected Maxwell model).

Presently, complex networked systems [14–19], received remarkable attention, are being studied across more and more significant fields of science and engineering [20]. A complex network can be seen as a large set composed of thousands of nodes linked together by edges, in which a node is a fundamental unit. The ubiquity of various real and artificial networks naturally motivates the current intensive study of fundamental theory and applications of complex networks. On the other hand, the flow behavior of polymer melts seems to be dominated by the entanglement phenomenon. It is a common assumption to consider the polymer molecules in a melt to be organized in a network of the entanglements that are temporary junctions. Therefore, we are able to consider polymer melts as an undirected complex network with a community structure, the entanglements in the polymer melts as the nodes while polymer chains as the communities. In 2009, Zhang [21] has been constructed an evolving network model with community structures to describe the entangled network structure in polymer melts visually.

In this paper, we review the research on entangled network models of polymer melts from three aspects, which are kinetic network, affine and nonaffine transient network, and complex network, respectively.

2. Kinetic network

In kinetic network theories, the flow-field-dependence is imparted through a hypothesis for the rate of destruction and reformation of entanglements in the material. These hypotheses are kinetic rate equations, which can be solved to predict the flow-induced change in the structure of the material. The transient structure can be made to depend on the invariants of the rate of deformation tensor or the invariants of the extra stress tensor. This theory is based on the concept of flow induced structure variation, controlled by the simultaneous existence of entanglement loss and regeneration. When steady state is attained, both processes occur at the same rate and the entanglement density of the fluid remains constant with time. Under transient flow conditions, the fluid structure becomes time dependent as a result of unequal rates of the two competing processes affecting entanglement density. The viscoelastic response of the fluid is, in turn, influenced by the varying structural state.

Marucci et al. [2] modeled these entanglements as temporary junctions whose kinetics is governed by invariants of the extra stress tensor and thermal motion of the molecules. The Marucci model is:

$$\frac{dx_i}{dt} = \frac{(1-x_i)}{\lambda_i} - \frac{a}{\lambda_i G_i} [-x_i II(\tau_i)]^{\frac{1}{2}} \quad (1)$$

where G_i and λ_i are the relaxation modulus and time of the i th spectral element at equilibrium, and they depend on a scalar structural parameter x_i , which named entanglement density with ranging from 0 to 1, in the manner as:

$G_i = G_{0i} x_i$, $\lambda_i = \lambda_{0i} x_i^{1.4}$, where λ_{0i} and G_{0i} are the relaxation time and modulus of the i th spectral element at equilibrium. The dimensionless nonlinear parameter a is obtained by fitting the model to steady shear viscosity data, and $II(\tau_i)$ denotes the second invariant of the i th spectral component of the extra stress tensor. The first term on the right of Eq.(1) governs the creation of the entanglements, while the second governs the destruction of entanglements. Apparently, this model has no nonlinear transient parameter to fit transient nonlinear flow.

Since the advent of Marrucci's model, several other kinetic rate equations have been proposed. The Acier's model [3] is:

$$\frac{dx_i}{dt} = \frac{(1-x_i)}{\lambda_i} - \frac{ax_i}{\lambda_i} - \left[\frac{tr \tau_i}{2G_i} \right]^{\frac{1}{2}} \quad (2)$$

where $tr(\tau_i)$ is the trace of the i th spectral component of the extra stress tensor. Eq. (1) and Eq. (2) attempt to explain the nonlinear viscoelastic behavior using a discretization of the linear relaxation spectrum (G_{0i}, λ_{0i}), moreover there is only one nonlinear parameter a , so it is ill-considered using the steady shear viscosity curve to predict the nonlinear transient behavior without fitting nonlinear transient measurements.

In 1982, the Mewis-Cleyn model [22] was proposed:

$$\frac{dx_i}{dt} = \frac{k_1(1-x_i)}{\lambda_i^m} - k_2 x_i [-4II_D]^{m/2} \quad (3)$$

where k_1 is a dimensional rate constant for the creation of entanglements by thermal diffusion, k_2 is a dimensional

rate constant for the destruction of entanglements due to shear, and m is a dimensionless elastic parameter, which is typically between 0.8 and 0.9 for polymer melts. But this model did not appear to reduce to linear viscoelasticity.

The Mewis-Denn model [6] is:

$$\frac{dx_i}{dt} = \frac{k_1(1-x_i)}{\lambda_i^m} - \frac{k_2x_i}{\lambda_i^m} \left[\frac{tr\tau_i}{2G_i} \right]^m \quad (4)$$

When $m=1$ and $k_1=1$, this model reduces to the Acier's model with $k_2=a$.

The Moldenaers-Mewis model [23–24] is:

$$\frac{dx_i}{dt} = \frac{A_0[1+k(-II_D)^{1/2}]}{\lambda_i^{0.3}} \left[\frac{1}{1+a[tr\tau_i/2G_i]^{1/2}} - x_i \right] \quad (5)$$

This model successfully modeled the tensile start-up behavior of the branched low density polyethylene.

The Berkeley model [25–26] is:

$$\frac{dx_i}{dt} = \frac{k_1(1-x_i)}{\lambda_i^m} - k_2x_i[-II(D)]^{\frac{m}{2}} (1 - e^{-\lambda_i}[-II(D)]^{\frac{m}{2}}) \quad (6)$$

where $II(D) = 2tr(D^2)$ is the second invariant of the stress rate, $D = (\nabla v + \nabla v^T)/2$ is the rate of deformation tensor with velocity gradient tensor ∇v . This model assumed that the rate of destruction of entanglements depends of the rate of deformation tensor rather than the stress tensor. It was shown to work well for polymer solutions in simple shear, stress growth, stress relaxation, step shear, and vibration shear [27], but was not tested in extensional flow.

The Liu model [5, 28] is:

$$\frac{dx_i}{dt} = \frac{k_1(1-x_i)}{\lambda_i^m} - k_2x_i[-II(D)]^{\frac{m}{2}} \quad (7)$$

Unlike the previous kinetic models, in this model they defined $G_i = G_{0i}$ and $\lambda_i = \lambda_{0i}x_i$. When $m=1$, Eq. (7) is the simplification of the Liu model, which has only two parameters; one for thermal regeneration and the other for shear induced breakdown of structure.

The DE KEE model [29–30] is:

$$\frac{dx_i}{dt} = k_c(1-x_i) + (k_1f_2 - k_1f_1)x_i \quad (8)$$

where k_c is a creation rate constant and represents the rate of creation due to diffusion, k_1 is a constant which represents the rate of creation due to the applied shear rate, k_1 is a loss rate constant, f_1 and f_2 are arbitrary functions. This model can predict shear thinning, shear thickening, thixotropy, and antithixotropy in different ranges of shear rates. There are two apparent points different from the Liu's model: one is that the rates of creation and destruction are function of the shear rate, the other is that the relaxation time is not proportional to the viscosity and is time independent.

3. Affine and nonaffine transient network

A versatile transient network theory can be used as a framework for the interpretation of the large amplitude oscillatory shear behavior of polymer melts in terms of their entanglement kinetics.

Giacomin and coworkers [8–9, 31–32] used the upper convected Maxwell equation with a kinetic rate equation to interpret the large amplitude oscillatory shear behavior of seven molten polyolefins. From Giacomin's research, there is only the Mewis-Denn model and the Liu model can give better fit for the experimental data in the large amplitude oscillatory shear field. Since the simplified Liu model has only two parameters, it provides a simpler framework for interpreting the viscoelastic behavior in the large amplitude oscillatory shear field. Simultaneity, determining the kinetic rate constants k_1 and k_2 has heretofore been tedious. In Reference [31], Jeyaseelan and Giacomin offered a less tedious method to determine them. In fact, most of parameters in the model can be determined by fitting the model to steady shear viscosity data, the spectrum (G_i, λ_i) can be evaluated from a small amplitude oscillatory shear test.

In Giacomin's research, it is a common assumption to consider the network and the liquid undergoing identical

deformation that is so-called affine network deformation. But for the polymer melts in large amplitude oscillatory shear, macroscopic network deforms differently from the liquid that is so called nonaffine network deformation. In 1978, Phan-Thien[33] proposed a nonaffine differential constitutive equation to describe the viscoelastic behavior of polymer melts. In 1984, Larson [34] proposed a network strand theory to describe the nonaffine deformation of polymer melts. In 1994, Giacomin [32] concluded that both two models could not describe accurately the nonaffine deformation of LDPE in large amplitude oscillatory shear. At the same time, Giacomin studied on the rheology of LDPE melt with the revised upper convected Maxwell model in large amplitude oscillatory shear, but it is only under severer conditions of strain amplitude and frequency in which the nonaffine deformation is clearly visible, and the nonaffine deformation is very small.

In 2004, Zhang[10–13] has proposed the nonaffine model (the Gordon-Schowalter convected Maxwell model). For a large amplitude oscillatory shear experiment, Zhang's kinetic rate equation in oscillatory shear is:

$$\frac{dx_i}{dt} = \frac{k_1(1-x_i)}{\lambda_i} - k_2\gamma_0\omega|\cos\omega t|x_i = \frac{k_1(1-x_i)}{\lambda_{0i}\left(\frac{x_i+\alpha}{1+\alpha}\right)^{1.4}} - k_2\gamma_0\omega|\cos\omega t|x_i \quad (9)$$

For a parallel superposition vibration force field upon steady shear flow, the imposed shear rate is $\dot{\gamma} = \dot{\gamma}_m + \gamma_0\omega\cos\omega t$, where $\dot{\gamma}_m$ is the shear rate that is no longer a function of time in steady state. So Zhang's kinetic rate equation ($m=1$) in parallel superposition vibration force field upon steady shear is:

$$\frac{dx_i}{dt} = \frac{k_1(x_m - x_i)}{\lambda_i} - k_2\Delta\dot{\gamma}x_i \quad (10)$$

where $\Delta\dot{\gamma} = \gamma_0\omega\cos\omega t$ is the net shear rate after imposing parallel superposition vibration force field upon steady shear flow, x_m is the entanglement density in the steady state.

From Zhang's result, the nonaffine transient network theory can be used for the interpretation of the rheological behavior of molten polymer in vibration force field, and the accurate precision of it is higher than that of the affine network model (the upper convected Maxwell model), and the effect of the vibration parameters on the shear stress and entanglement density can also be considered.

4. Complex network model

In the complex network model [21], we consider polymer melts as an undirected complex network with a community structure, the entanglements in the polymer melts as the nodes while polymer chains as the communities, and the entanglements of the same chain are inner-nodes, two different chains entangle to create an inter-node. We initialize our network model with M ($M > 1$) communities, in each of which there are m_0 ($m_0 > 1$) fully connected nodes. For simplicity, the model is both undirected and unweighted. The basic rules of the model are described as follows:

1. Growth: At each time step, only one of the following three cases can be worked:

- (1) With probability α , a new node is added, which first chooses a community to add into. Then it connects m existing nodes in this network. Each one of those m nodes is chosen from its own community with probability q ($0 \leq q \leq 1$) and from other communities with probability $1-q$.
- (2) With probability β , a new community containing m_0 fully connected nodes is added. Then we randomly choose one node in the new community to connect m nodes in other already existing communities following the preferential attachment mechanisms.
- (3) With probability γ ($\gamma = 1 - \alpha - \beta \geq 0$), a new node and a new community containing m_0 fully connected nodes are added at the same time step. Then they connect with others under the rule shown in the above two cases.

It's necessary to point out that when a new node chooses an inter-community neighbor, it firstly chooses a community and then chooses one node from that community. Although one certain community could be chosen for more than one time, multiple links to the same node are not permitted.

2. Preferential attachment:

- (a) Community size preferential attachment: When a new node chooses an existing community to add (or chooses another community from which to get an inter-community neighbor), we assume the probability $P(S_i)$ [20]

that it will choose community i depends on the size S_i of community i , such that:

$$P(S_i) = \frac{S_i}{\sum_i S_i}. \quad (11)$$

- (b) Inner-community preferential attachment: when choosing a neighbor in the same community (denoted as the j th community) to which the new node is connected through inner-community link, we assume that $P(k_{ij}^1)$ is the probability the new node will be connected to node i in community j depending on the inner-degree k_{ij}^1 (defined as the number of inner-community links connected to node i) in such a way that:

$$P(k_{ij}^1) = \frac{k_{ij}^1 + 1}{\sum_i (k_{ij}^1 + 1)}. \quad (12)$$

- (c) Inter-community preferential attachment: when choosing a node from the other communities (denoted as g ($g \neq j$) community) to which the new node is connected through inter-community link, we assume that $P(k_{ig}^2)$ is the probability the new node will be connected to node i in community g depending on the inter-degree k_{ig}^2 (defined as the number of inter-community links connected to that particular node) in such a way that:

$$P(k_{ig}^2) = \frac{k_{ig}^2 + 1}{\sum_i (k_{ig}^2 + 1)}. \quad (13)$$

Based on the community size, the inner- and inter-community preferential attachments, which yields scale-free networks having power-law distributions of the inner-degree, inter-degree and total degree. Our theoretical analysis of the distributions can also be done similarly to that in Ref. [35].

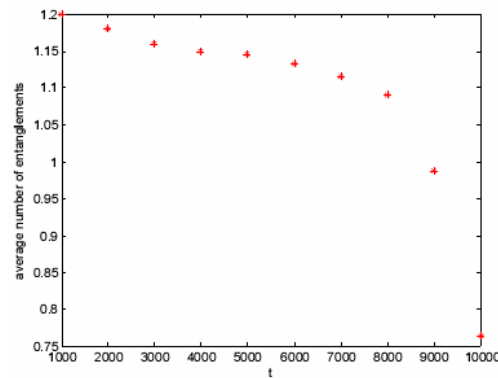


Fig1. The average number of entanglements of the present model versus time step t

$\gamma = 2E/N$ is defined to be the average number of entanglements, where N is the total number of nodes, and E is the number of edges. In Fig.1, we present simulation results for the average number of entanglements vs. the time step t when $\alpha = 0.45$, $\beta = 0.05$, $\gamma = 0.5$, $q = 0.9$, that is, the average number of entanglements decreases. This result is significant to the application of our model. If the number of entanglements decreases, the number of vacant sites of polymer melts increases, the force between molecules decreases, and the effect of the molecular orientation becomes stronger which results in the material tensile strength and stiffness increasing. In other words, it is in favor of the reptation of molecular quickly, and the viscosity decreases. Therefore, it is easy to process the polymer products. Actually, in real processing, we often make the viscosity of polymer melts decreased by technical approaches such as heating or adding pressure. In summary, our model materializes these properties of polymer melts.

5. Conclusion

We review the research on entangled network models of polymer melts from three sides. The classical kinetic network models can not describe the rheological behavior of polymer melts in vibration force field accurately, the nonaffine transient network structural model can describe the nonlinear viscoelastic behavior of polymer melts under vibration force field more accurately than affine model. It is remarkable that the rheology of the entangled polymer melts can be discussed by complex network model. In the near future, we will study how to control the macroscopic material response by analyzing the characteristics of the complex network models.

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